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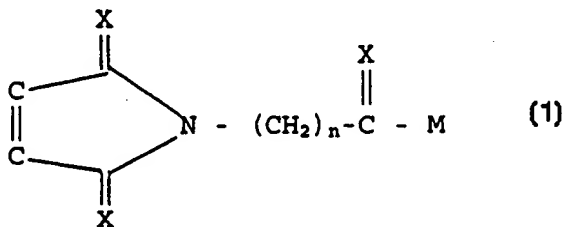
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(54) Title: PROCESS FOR THE PREPARATION OF A MALEIMIDE COMPOUND, MALEIMIDE COMPOUND, RADIATION-CURABLE COMPOSITIONS COMPRISING SAID COMPOUND AND COATED PRODUCTS

(57) Abstract

The invention relates to a process for the preparation of a maleimide compound comprising the steps of (i) reacting a compound according to formula (1) wherein M is halogen or alkoxylate, and each X, independently, is O or S, with a compound (2) comprising a backbone and having at least 1 group per molecule, capable of reacting with the compound according to formula (1), and (ii) obtaining the maleimide compound.



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5 PROCESS FOR THE PREPARATION OF A MALEIMIDE COMPOUND,
 MALEIMIDE COMPOUND, RADIATION-CURABLE COMPOSITIONS
 COMPRISING SAID COMPOUND AND COATED PRODUCTS.

10 The invention relates to a synthetic route
for making maleimide compounds. The invention further
relates to certain maleimide compounds per se and to
radiation curable compositions comprising said
maleimide compounds. Finally, the invention relates to
the coated products.

15 WO 98/07759 describes mono- and
multifunctional aliphatic maleimides,
photopolymerization methods using said maleimides and
photopolymerizable compositions comprising said
maleimides. WO 98/07759 also discloses the synthesis of
20 several functionalized maleimide compounds derived from
an hydroxy-functional compound (further called the OH-
route). However, it appears that the synthesis of
maleimides is generally cumbersome, several of these
maleimide compounds are not easy to synthesise through
25 the so-called OH-route and are therefore, not easy
accessible. Only a few maleimide compounds are readily
available.

 Moreover, the maleimide compounds known
from WO 98/07759 are all hydrocarbon substituted.
30 However, hydrocarbon functional maleimide compounds
appear to be not well compatible with other components
that are generally used in radiation-curable
composition.

 With the aid of maleimide compounds it
35 appears possible to induce photopolymerisation without
the need of conventional photoinitiators or
sensitizers, or, with a lower amount of photoinitiator.

Because most of the ethylenically unsaturated bonds of the maleimide are consumed during photopolymerisation, this photopolymerisation-inducing compound is built into the polymer network, and no residual maleimide based chromophores are left. Hence, the resulting radiation cured compositions are relatively stable, in particular with respect to light induced aging. Despite these potentially attractive characteristics, several disadvantages still are apparent. In particular, the maleimides described in the prior art are derived from N-methylol maleimide (N-hydroxymethyl maleimide) which is a very toxic compound. If the maleimide compound hydrolyses, this results in the release of the toxic alcohol compound. Furthermore, the maleimides described in the prior art exhibit a relatively slow cure.

It is an object of the present invention to find a suitable and easier synthesis route to several maleimide compounds.

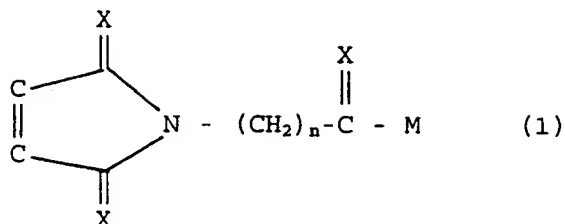
It is another object of the present invention to provide maleimide compounds that show an improved compatibility with the remaining components of the composition.

It is a further object of the invention to provide maleimide compounds that exhibit fast cure speed induction on photopolymerisation and a decreased amount of extractables.

One or more of these objects are achieved by a process for the preparation of a maleimide compound comprising the steps of

(i) reacting a compound according to formula (1)

5



- wherein M is halogen or alkoxylate, and each X,
 10 independently, is O or S,
 with
 a compound (2) comprising a backbone and having at
 least 1 group per molecule, capable of reacting with
 the compound according to formula (1), and
 15 (ii) obtaining the maleimide compound.

The maleimide compound obtained by the
 process according to the present invention can be mono-
 or multifunctional.

- The present invention provides an easy
 20 synthetic method for making a variety of mono- and
 multifunctional maleimide compounds. A further
 advantage of the synthetic method of the present
 invention is the great versatility, since the maleimide
 synthesis is performed before attachment to different
 25 backbones.

- The unsaturated bond of the maleimide
 preferably is unsubstituted. However, the maleimide may
 be substituted with one alkyl or aryl group with 1-6
 carbon atoms. Hence, the unsaturated bond of the
 30 maleimide in the formulae of this application can be
 denoted as $\text{HC} = \text{CR}^4$ wherein R^4 can be hydrogen or an
 alkyl or aryl group with 1-6 carbon atoms. If both
 hydrogens would be alkyl groups, the cure speed
 severely lowers or, the maleimide compound does not
 35 polymerise due to steric hindrance. Hence, the

compounds depicted in the formulae encompass the at one carbon atom substituted compounds.

In one particularly preferred embodiment X is oxygen and M is as defined above.

5 Suitable examples for M being a halogen are Cl, Br, and I; for M being an alkoxylate, examples include ethoxy, propoxy, t-butoxy, tert-butoxy carbonylate, substituted phenoxy and hydroxy succimide.

 Preferably, the compound according to
10 formula (1) is the acid-chloride functional maleimide-compound. The compound according to formula (1) for example is capable to react with compounds having hydroxy, thiol or amine functionality.

 Compounds according to formula (1) can be
15 obtained by suitable synthesis methods, for example such as described in L. Paul et al.; Chem. Ber. 100 2757-2760 (1967). However, this reference only describes the synthesis of a monofunctional maleimide compound (with 1 methylene between the maleimide group
20 and the functional group) via the reaction between an acid chloride functional maleimide compound and an aminophenyl. However, the present invention is directed to maleimide compounds (ii), with the exception of a monofunctional maleimide compound having an aromatic
25 amine as functional group, because aromatic amine groups include yellowing.

 The reaction between the compound according to formula (1) and the compound (2) is preferably performed at a temperature range between -30°C and +80°C
30 in (a suitable) organic solvent such as tetrahydrofuran, dichloromethane, pyridine, diethylether, toluene, esters, carbonates and the like. The reaction can also be performed in mixtures of the

above mentioned organic solvents. Preferably, ester-based organic solvents are used, such as dimethylcarbonate, which increases the yield of the reaction. In another preferred embodiment, the reaction
5 of the acid chloride functionalised maleimide with hydroxy functional groups is performed in equimolar amounts of tetrahydrofuran and pyridine below 0°C.

Further, hindered phenol-type stabilisers preferably are added to the reaction mixture to avoid
10 polymerisation of the maleimide group at elevated temperatures. Preferably, t-butyl catechol is used as stabiliser.

Moreover, the reaction generally is performed in the absence of water and in the presence
15 of base.

The present process can be used to synthesise mono- and multifunctional maleimides.

First, there are several preferred embodiments for the preparation of the monofunctional
20 maleimide compounds according to the present invention.

One of the preferred embodiments according to the present invention is directed to the process for the preparation of monofunctional maleimide compounds wherein n equals 1 and wherein the backbone is not
25 comprising benzophenone, a succinimide or phenyl group.

Another preferred embodiment of the process according to the present invention is the preparation of monofunctional maleimide compounds wherein n is greater than 1 and wherein said backbone has a
30 molecular weight higher than 169 and is not comprising an anhydride or cyclodextrine group.

Second, there are several preferred embodiments for the preparation of the multifunctional

maleimide compounds according to the present invention.

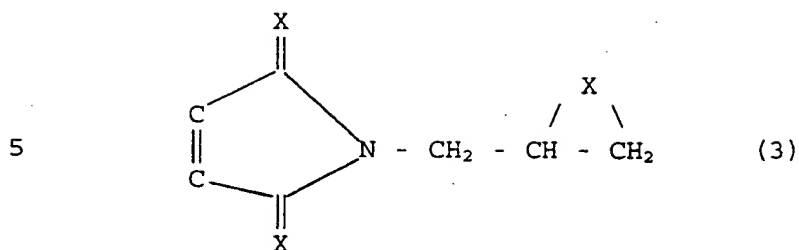
Multifunctional aliphatic maleimide compounds are known as such from WO-A-98/11141, EP-A-241133 and EP-A1-878482. Both synthesis methods suffer
5 from a lack of versatility in making a large variety of compounds. Also, maleic and fumaric amid acids will be present due to incomplete imidisation. However, the products obtained by the process according to the present invention contain maximum 6 wt.% of impurities
10 such as not ring-closed maleimide by-products. Therefore, our technique results in an improved combination of purification and % yield.

One of the preferred embodiments according to the present invention is directed to the process for
15 the preparation of multifunctional maleimide compounds wherein n equals 1. The hydrogens of the CH₂ group next to two non-aliphatic groups are relatively labile, thereby increased cure speed is caused.

Another preferred embodiment of the process
20 according to the present invention is the preparation of multifunctional maleimide compounds wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 150 and does not comprise a nitrogen containing phenyl group.

25 Another synthetic pathway for making mono- and multifunctional maleimide compounds according to the present invention is a process for the preparation of a maleimide compound comprising the steps of

(i) reacting a compound according to formula (3)



10 wherein X, independently, is O or S,
with

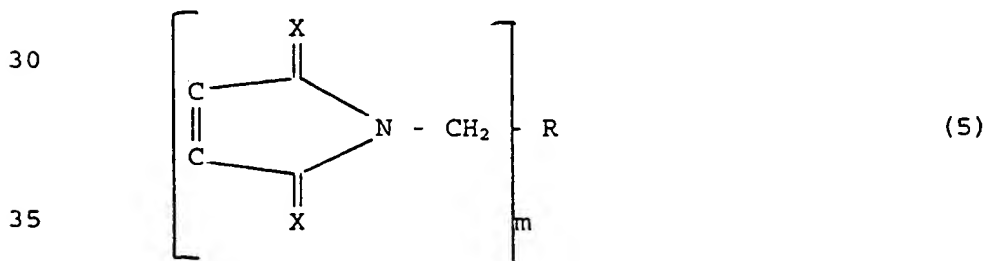
a compound (4) having at least on average 1 group per molecule, capable of reacting with the compound according to formula (3) and

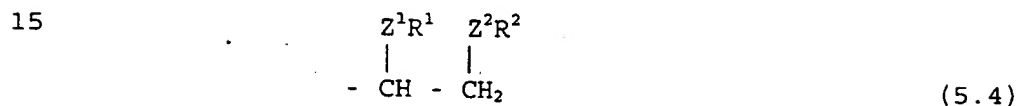
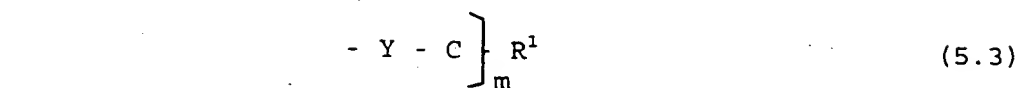
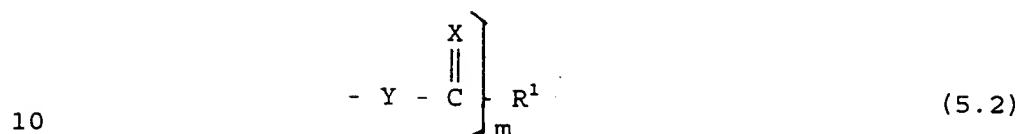
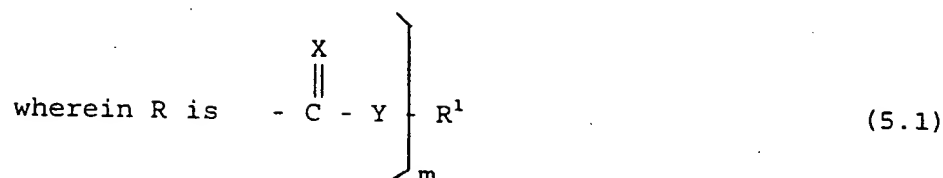
15 (ii) obtaining the maleimide compound.

The compound according to formula (3) for example is capable of reacting with carboxylic acid, hydroxy, thiol, phosphine, amine and phosphoric acid functionality.

20 Compounds according to formula (3) can be obtained by suitable synthesis methods, for example such as described in T. Kurosaki et al.; J. Phot. Sc. 36 122-124 (1988).

Maleimide group comprising compounds
25 according to the invention and exemplified by formula (3) appear to be very efficient for the induction of photopolymerisation of for example (meth)acrylates, even in the absence of any other photoinitiator:





wherein

20 m is at least 1,

each X , independently, is 0 or 5

Y is O, S or NH

25 Z¹ and Z² independently designate for O, S, or NR³, and wherein R¹, R² and R³ can be, independently, hydrogen or an organic group and wherein R¹, or at least R¹ or R² is the remainder of the backbone of the multifunctional maleimide compound.

In one particularly preferred embodiment X is oxygen and Y is as defined above. Most preferably, Y is O or NH; and R' is the remainder of the molecule.

The maleimide groups are attached via the functional group to the remainder of the molecule (R' , R^1 or R^2), further in this application also called the backbone.

35 The backbone (R' , R^1 or R^2) can be any
suitable organic molecule. In particular, a distinction
can be made between two classes of organic
molecules/backbones.

A first class of backbones are reactive backbones; in particular, these backbones comprise one or more groups that are reactive in the photopolymerisation process. The active site of such group can be a photoinitiating molecule, a co-initiator or sensitizer, a polymerizable, ethylenically unsaturated group, and the like. Suitable examples of the active sites are benzophenone, thioxanthone, an aliphatic tertiary amine, a (meth)acrylate, a vinyl ether and the like. Most preferably, no aromatic amines are used. Maleimide compounds with an aromatic amine group have a tendency to yellow.

A second class of organic backbones comprises molecules that are non-reactive towards the photopolymerisation process. The non-reactive backbone molecule can be of low or high molecular weight. The molecular weight of the non-reactive groups will generally be higher than 14 and lower than 90,000. Preferably, the molecular weight will be higher than 50 and lower than 50,000. Most preferably, higher than 100 and lower than 10,000. This class comprises lower molecular weight groups such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, cyclohexyl, phenyl, bisphenyl, substituted phenyl and the like. Moreover, the higher molecular weight groups can be any organic groups such as hydrocarbons, oligoesters, oligoethers, oligocarbonates, oligourethanes, oligoimides, oligoamides, oligoacrylates and the like. The term "oligo" refers to oligomers having at least two repeating units and includes also the "poly"mers.

Suitable backbone molecules of the monofunctional maleimide compounds can be derived from hydroxy or aminofunctional molecules such as, for example, from trimethylolpropane diacrylate,

pentaerythritol triacrylate, monohydroxy functional polyethyleneglycol, monohydroxy functional polypropyleneglycol, mono-amino functional polyethers, available as Jeffamine®, hydroxy acids and the like.

5 Suitable backbone molecules for the multifunctional maleimide compounds can be derived from hydroxy or aminefunctional molecules such as, for example, from trimethylolpropane, pentaerythritol, dipentaerythritol, amine functional dendrimers like
10 Astramol®, polyethyleneglycol, polypropylene-glycol, amine functional polyesters, available as Jeffamine®, acid or hydroxyfunctional polyesters derived from diols, diacids and/or hydroxy acids, acid, amino or hydroxyfunctional acrylic polymers, isophorone
15 diisocyanate, toluene diisocyanate, and trimerisation products therefrom, polycarbonate-diols, and the like.

 Preferred backbone molecules are polyethers, ethoxylated compounds, and polyurethanes. In particular, trimethylol propane, ethoxylated
20 trimethylol propane, propoxylated trimethylol propane, pentaerythritol, ethoxylated pentaerythritol, glycerol, propoxylated glycerol, polytetrahydrofuran, polyethylene oxide, polypropylene oxide, and tert-amine bearing backbones.

25 The molecular weight of the maleimide compound (ii) will generally be higher than 159 and lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation curable
30 composition. The molecular weight as used herein is (for oligomeric compounds) the number average molecular weight, as determined by Gel Permeation Chromatography (GPC) with polystyrene standards.

The number of maleimide groups per molecule can vary from one up to 20, preferably from 1 up to 10, more preferred from 1 up to 5.

5 The number of carbon atoms n between the maleimide and the carbonyl can be 1, 2 or higher. Generally, n will be lower than 20, preferably lower than 10. The alkylene group is aliphatic, and preferably is a straight chain alkylene, but it may comprise a cyclic group. Suitable examples include
10 ethylene, 1,3-propylene, 1,2-propylene, methylcyclohexylene, 1,3-*t*-butylene, 1,5-pentylene and the like. Compounds with maleimide functional groups with only one methylene carbon spacer between a functional group and the maleimide chromophore are
15 particularly cumbersome to synthesise.

The maleimide compound according to this invention preferably has an ester, thioester, carbonate, ether, urethane, amine, amide or imide as the functional group. Most preferably, an ester
20 functional group.

In one preferred embodiment of the maleimide compound of the invention, the maleimide compound according to formula (5) is monofunctional ($m=1$).

25 The molecular weight of the monofunctional maleimide compound will generally be higher than 159, preferably higher than 173 and in particular higher than 250. Higher molecular weight maleimide compounds are generally better compatible with the other
30 constituents of the radiation curable coating composition. However, low molecular weight compounds can be made compatible by varying the R-group functionality.

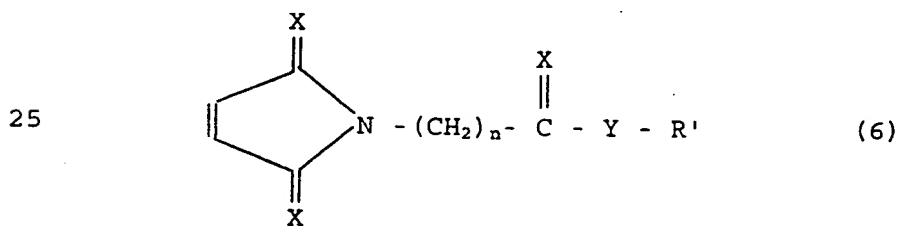
The molecular weight of the monofunctional

maleimide compound generally will be lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation curable composition. Preferably, the molecular weight will be lower than 10,000, more preferably, lower than 5000, and particularly preferred below about 1000 because such molecular weights make it more easy to formulate radiation curable compositions without non-reactive diluents.

The monofunctional maleimide compound according to this invention preferably has an ester, thioester, ether, amide, imide or amine as the functional group. More preferably, an ester, thioester or amide functional group, most preferably, an ester functional group.

Monofunctional maleimide compounds according to formula (5), with the exception of R' being an aromatic amine, are novel.

Preferred monofunctional maleimide compounds are compounds according to formula (6)



wherein Y is O, S or NH;
 each X, independently, is O or S; and
 R' is the remainder of the backbone, and wherein
 (i) n equals 1 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and not comprising benzophenone, a succinimide or anhydride group, or

(ii) n equals 2 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and said backbone is not comprising a diol-substituted alkane, a succinimide, anhydride or cyclodextrine group, or

(iii) n is at least 3.

In a second preferred embodiment of the maleimide compound of the invention, the maleimide compound according to formula (5) is multifunctional (m>1).

Preferably, the multifunctional maleimide compound has a functionality of 1.9 or higher, in particular 2.5 or higher, as a higher functionality appears to improve cure speed and to give cured products with lower photoinitiator based extractables.

The upper limit of the functionality seems to be non-critical, and the functionality will be in general lower than 20, preferably lower than 10 and in particular will be about 5 or lower.

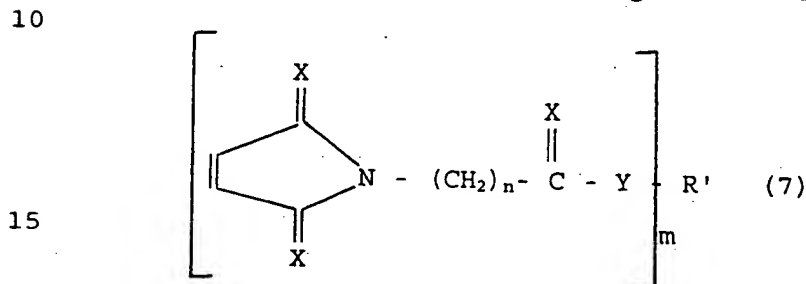
The molecular weight of the multifunctional maleimide compound will generally be higher than 250, preferably higher than 325 and in particular higher than 400. The molecular weight of the multifunctional maleimide compound generally will be lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation curable composition. Preferably, the molecular weight will be lower than 50,000, more preferably lower than 10,000, particularly preferred below about 10,000 and most preferred below about 5,000 because such molecular weights make it more easy to formulate radiation curable compositions without non-reactive diluents.

The multifunctional maleimide compound

according to this invention preferably has an ester, thioester, carbonate, ether, urethane, amine, amide or imide as the functional group. Most preferably, an ester functional group.

5 Multifunctional compounds according to formulae (5) are novel, excluding phenolic group comprising backbones for formula (5.4).

Preferred multifunctional maleimide compounds are compounds according to formula (7)



wherein each X, independently, is O or S,
Y is O, S or NH,

20 R' is the remainder of the backbone, and m is - on average - 1.6 or higher, and wherein

(i) n equals 1 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons, or

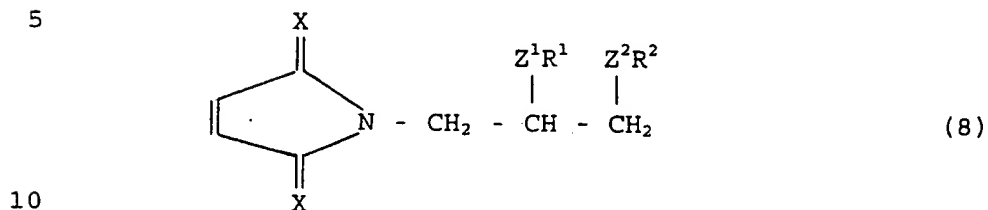
(ii) n is at least 2 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)ether, (oligo)ester, (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent

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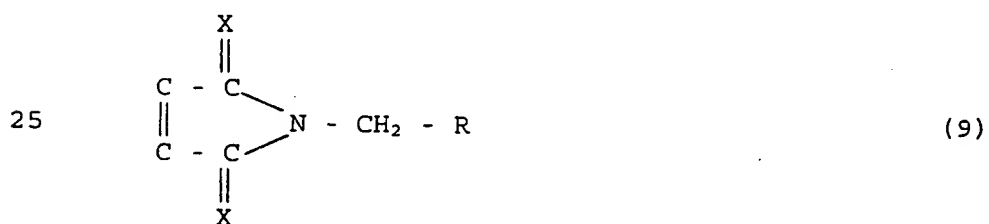
carbons.

Furthermore, the present invention also relates to maleimide compounds according to formula (8)

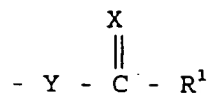


comprising at least one maleimide group, wherein X is O or S, and Z¹ and Z² independently designate for O, S, or NR³, and wherein R¹, R² and R³ can be, independently, hydrogen or an organic group and wherein at least R¹ or R² is the remainder of the molecule. The maleimide compounds according to formula (8) can be mono- or multifunctional.

Other preferred multifunctional maleimide compounds are the ones depicted by formula (9)



30 wherein R is



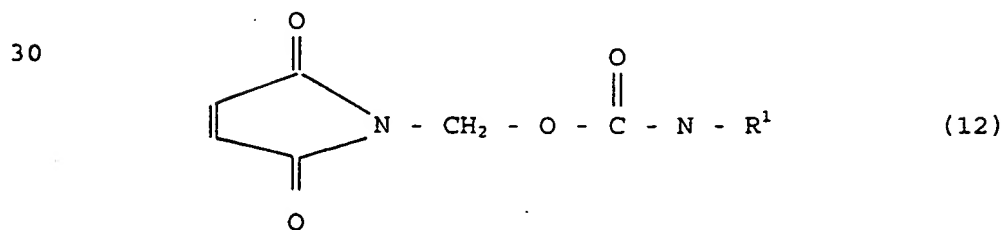
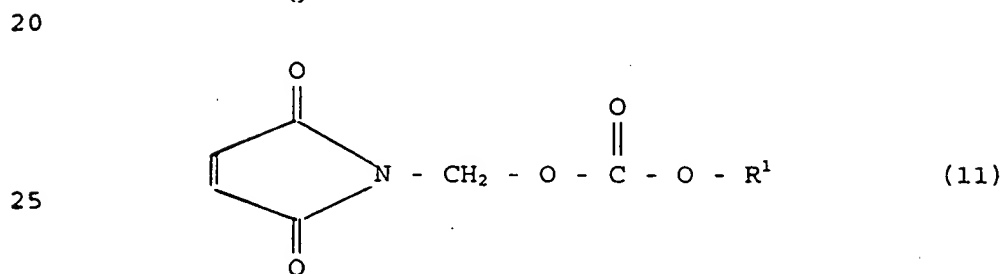
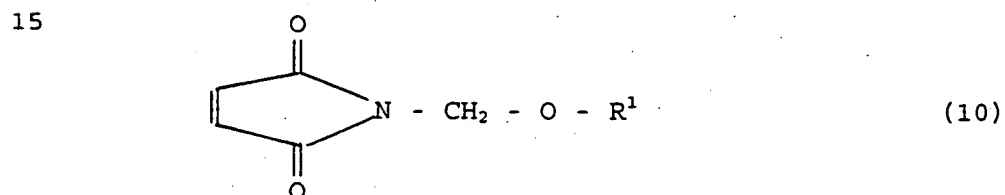
wherein

each X, independently, is O or S

Y is O, S or NH, and

10 wherein R¹ is the remainder of the backbone of the multifunctional maleimide compound.

Especially preferred are the ones wherein X and Y are O and are depicted by formulae (10) to (12)



35

Further, the present invention relates to a radiation-curable composition comprising

a) at least one compound having ethylenically

unsaturated bonds other than those in
maleimide groups as defined under (b)

- b) at least one maleimide compound according
to formula (6), (7) or (8) wherein

- 5 Y is O, S or NH,
each X, independently, is O or S,
m is - on average - 1.6 or higher,
R' is the remainder of the molecule,
Z¹ and Z² independently designate for O, S, or NR³, and
10 wherein R¹, R² and R³ can be, independently, hydrogen or
an organic group and wherein at least R¹ or R² is the
remainder of the molecule.

In one preferred embodiment of the
radiation curable composition according to the present
15 invention, the monofunctional maleimide compound
according to formula (6) is further characterised by

- (i) n equals 1 and R' is an organic
backbone being non-reactive towards the
photopolymerization process, said backbone comprising
20 hydrogen, carbon and at least one of O, S, or N, and
not comprising a succinimide or anhydride group, or

- (ii) n equals 2 and R' is an organic
backbone comprising hydrogen, carbon and at least one
of O, S, or N, and said backbone is not comprising a
25 diol-substituted alkane, a succinimide, anhydride or
cyclodextrine group, or

- (iii) n is at least 3.

In a second preferred embodiment of the
radiation curable composition according to the present
30 invention, the multifunctional maleimide compound
according to formula (7) is further characterised by

- (i) n equals 1 and R' comprises a
hydrocarbon backbone having a molecular weight higher
than 150, an (oligo)carbonate, (oligo)urethane,

(oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons, or

- 5 (ii) n is at least 2 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)ether, (oligo)ester, (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures
10 thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons.

In a third preferred embodiment of the radiation curable composition according to the present
15 invention, the maleimide compound according to formula (8) is further characterised by comprising at least one maleimide group.

The present invention also relates to radiation-curable composition comprising

- 20 a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b)
b) at least one multifunctional maleimide compound having at least 2 maleimide groups according
25 to formula (9).

Preferably, the radiation curable composition according to the present invention comprises a maleimide compound (b) as defined above wherein X is oxygen.

- 30 The maleimide compound preferably is present in the radiation curable composition in an amount between 0.01-60 wt.%. More preferably, the monofunctional maleimide compound is present in the radiation curable composition between 0.1-50 wt.%, most

preferably between 0.1-20 wt.%.

More preferably, the multifunctional maleimide compound is present in the radiation curable composition in an amount between 0.1-20 wt.%.

5 Generally, the amount of maleimide groups is such, that the ratio of maleimide groups to other ethylenically unsaturated groups is 0.001 or higher, preferably 0.01 or higher. Generally, the amount of maleimide groups is 1 or lower with respect to the
10 other ethylenically unsaturated groups, preferably 0.5 or lower and particularly preferred 0.2 or lower.

The radiation curable composition comprises

- a) at least one compound having ethylenically unsaturated bonds other than those in the
15 maleimide groups of (b), and
b) the maleimide compound, being mono- or multifunctional.

The radiation curable composition of the present invention comprises (a) and (b); for purposes
20 of definition of wt. amounts, the total amount of (a) + (b) is 100 wt.%, and additional compounds that can be present are defined relative to the amount of (a) + (b).

Both compounds (a) and (b) can be mixtures
25 of compounds.

Examples of the ethylenically unsaturated group of compound (a) include (meth)acrylate, propenylether, vinylether, allylether, substituted or unsubstituted styrene, N-vinyl, fumarate, maleate,
30 itaconate, (meth)acrylamide, and mixtures of these.

Preferred ethylenically unsaturated groups are (meth)acrylate, N-vinyl, styrene and vinylether. Most preferred are (meth)acrylate functional compound.

The compound (a) preferably is a mixture of

oligomers and reactive diluents. Also preferred is a mixture of monofunctional and multifunctional compounds.

Examples of suitable oligomers comprise
5 (meth)acrylated polyesters, (meth)acrylated urethanes, (meth)acrylated epoxies, vinyl-ether functional urethanes and the like.

Examples of suitable reactive diluents are
lauryl (meth)acrylate, ethyl (meth)acrylate,
10 ethoxyethyl (meth)acrylate, phenoxyethyl (meth)acrylate, hexanedioldi (meth)acrylate, triethyleneglycol divinylether, trimethylol propanetri (meth)acrylate, isobornyl (meth)acrylate, N-vinyl-caprolactone, diethyleneglycol di (meth)acrylate,
15 cyclohexyldimethanol-di (meth)acrylate and the like.

In one embodiment of the invention, the radiation curable composition comprises electron rich and electron poor double bonds, as described in EP-A-618237 and W097/31981.

20 In another preferred embodiment, the composition comprises only electron-poor double bonds such as acrylates, fumarate compounds and the like.

The compositions comprising (a) and (b) are radiation curable as such. Nevertheless, cure speed can
25 be further improved using type-II (hydrogen abstraction) photoinitiators such as benzophenone, derivatives of benzophenone, such as substituted benzophenone, xanthone, thioxanthone, substituted thioxanthone and other xanthone derivatives,
30 anthraquinones, coumarines, in an amount between 0.1-10 wt.% (with respect to (a) + (b)). Type-II photoinitiators generally are used with an amine synergist. When using compound (b) according to the present invention, amine synergists are not necessary

in particular if curing is performed under a nitrogen atmosphere. Hence, preferable, amine synergists are present in an amount of less than 1 wt.%, and more preferably less than 0.1 wt.%. Nevertheless, amine synergist can be used up to 5 wt.% if useful in particular if curing is performed under an oxygen containing atmosphere, like in air.

Other examples of suitable photoinitiators are type I (α -cleavage) photoinitiators such as Darocure 1173 (2-hydroxy-2-methyl-1-phenylpropane-1-one as the active component), Irgacure 184 (hydroxy-cyclohexyl phenyl ketone as the active component), Irgacure 369 (2-benzyl-2-dimethylamino-1-(morpholinophenyl)-butanone-1 as the active component), and acylphosphines such as Lucerin TPO (2,4,6-trimethylbenzoyl diphenyl phosphine oxide). Chemical derivatives and combinations of these photoinitiators can also be used.

The radiation curable compositions can further comprise usual additives, colorants, fillers and the like, such as for example pigments, flow agents, stabilisers, antioxidants, slip agents, waxes, dyes, wetting agents, adhesion promoters, and the like.

The radiation-curable coating composition can be cured by different kinds of radiation, such as UV and EB radiation.

The most preferred irradiation source is ultraviolet light. Ultraviolet light is preferably high intensity light to provide a dosage to achieve reasonable curing rates. In the event that lower energy light is applied, it may then be desired to subject the compositions also to elevated temperatures in order to reduce the time for adequate polymerisation to occur.

With respect to UV-curing equipment we refer to, for example, pages 161-234 of Chemistry and Technology of UV and EB-formulations, Volume 1, Oldring 1991.

5 Suitable lamps employed to provide the desired high intensity and availablitiy of wavelength and spectral distribution include for example those available from Fusion Systems, Corp. Preferably, excimer lamps are used e.g. Fusion VIP 308.

10 The radiation-curable coating composition according to the invention can be used on different substrates, for example glass, paper, wood, plastic, metals such as aluminium and iron. An example of a glass substrate can be an optical glass fiber.

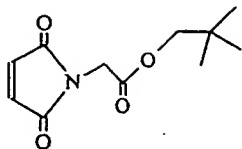
15 Finally, the present invention also relates to the products coated with a cured coating which coating before curing is a coating composition as described herein.

20 The invention will be elucidated with the following examples, without being limited thereto.

Examples I-VI are related to the preparation and characterisation of monofunctional maleimide compounds with 1 methylene spacer group between the maleimide
25 group and the functional group. Further, the use of said maleimides in the preparation of a radiation-curable composition is described.

Example I

30 Preparation of a monofunctional maleimide compound from neopentyl alcohol:



60 mmol 2,2-dimethyl-1-propanol and 60 mmol triethylamine were dissolved in 100 ml dry tetrahydrofuran. The mixture was cooled to 0°C and 84
5 mmol N-[(chloroformyl)methyl]maleimide dissolved in 50 ml tetrahydrofuran was slowly dropped to the solution. The reaction mixture was stirred overnight at room temperature. After filtration and evaporation, the brownish residue was dissolved in 150 ml dichloromethane
10 and washing with 60 ml 10% HCl and further washing three times with 60 ml water. Drying on sodium sulfate, filtration and evaporation yielded a yellow powder. After drying in a vacuum oven 42 mmol (73%) of a light yellow powder was obtained.

15

The structure was characterised by:

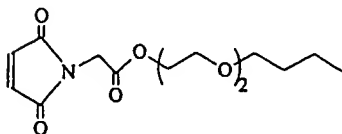
$^1\text{H-NMR}$ (CDCl_3) (δ/ppm): 6.8 (s, 2H); 4.3 (s, 2H); 3.85 (s, 2H); 0.95 (s, 9H)

IR, neat (frequency cm^{-1}): 1715 (C=O maleimide); 697
20 (C-H bend of maleimide double bond)

Example II

Preparation of a monofunctional maleimide compound from butyl carbitol:

25



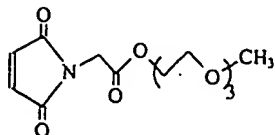
6.8g (42mmol) 2-(2-butoxyethoxy)ethanol was dissolved in 150ml THF. 7.0ml (50mmol) triethylamine and tert-butyl catechol were added. [In the synthesis examples, generally, between about 10 and about 50 mg of tert-butyl catechol is used.] The solution was cooled to -10°C and stirred thoroughly.

8.0g (46mmol) N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise in one hour. The reaction was stirred overnight at room temperature and filtered off. The clear brown filtrate was evaporated till an oil was obtained. Dissolving in dichloromethane and washing with water yielded 7.25g (24mmol, 57%) of a brown/orange oil.

15 $^1\text{H-NMR}$, CDCl_3 , (δ/ppm): 6.75 (s, 2H); 4.25 (t, 4H); 3.55 (3t, 8H); 1.5 (m, 2H); 1.3 (q, 2H); 0.85 (t, 3H)
IR, neat (frequency cm^{-1}): 1718 (C=O maleimide); 698 (C-H bend of maleimide double bond)

20 Example III

Preparation of a monofunctional maleimide compound from triethylene glycol monomethyl ether:



25 6.5g (40mmol) triethylene glycol monomethyl ether was dissolved in 100ml THF. 5.75ml (41mmol) triethylamine and tert-butyl catechol were added. The solution was

cooled down to -10°C and 7.0g (40mmol) of N-
[(chloroformyl)methyl] maleimide dissolved in 50ml THF
was added in 30 minutes. After stirring overnight at
room temperature, filtration and evaporation of the
5 THF, the dark liquid was dissolved in dichloromethane
and washed three times with water. The product was
collected as a orange/yellow oil with a yield of 6.8g
(22.5mmol, 56%).
¹H-NMR, CDCl₃ (δ/ppm): 6.8 (s, 2H); 4.3 (t, 4H);
10 3.65 (m&t, 10H); 3.9 (s, 3H)

Example IV

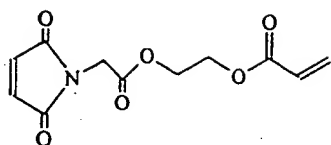
Preparation of a monofunctional maleimide
compound from 4-aminobenzophenone:

15

To a solution of 55mmol 4-aminobenzophenone in 250ml
THF, tert-butyl catechol and 60mmol triethylamine were
added. The solution was cooled down to -10°C.
55mmol N-[(chloroformyl)methyl] maleimide dissolved in
20 50ml THF was added dropwise. The reaction was stirred
at room temperature overnight and filtered off. The
filtrate was then evaporated and a solid product was
obtained. After washing with water and diethylether,
the product was dried under vacuum. This yielded 48mmol
25 (87%) of a white powder.

Example V

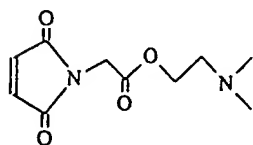
Preparation of a monofunctional (acrylate
functional) maleimide compound from 2-hydroxyethyl
30 acrylate:



To a 0°C solution of 5.75ml (50mmol) 2-hydroxyethyl
acrylate, tert-butyl catechol and 7.0ml (50mmol)
5 triethylamine 8.7g (50mmol) N-[(chloroformyl) methyl]
maleimide dissolved in 50ml THF was added dropwise. The
reaction was stirred at room temperature overnight.
Filtration and extraction with CH₂Cl₂/H₂O yielded an
orange oil which turns to solid in an ice/water bath.
10 3.0g (11.8mmol, 23%) of a light yellow/pale white
powder was obtained by crystallisation from cold ether.

Example VI

Preparation of a monofunctional maleimide
15 compound from dimethyl ethanolamine:



4.9g (55mmol) dimethyl ethanolamine and tert-butyl
catechol were dissolved in 200ml CH₂Cl₂ and cooled down
20 to 0°C. 9.6g (55mmol) N-[(chloroformyl) methyl]
maleimide dissolved in 40ml dichloromethane was added
dropwise. The suspension was stirred overnight at room
temperature and quenched with 2.17g (54mmol) NaOH_(aq).
Separation of the water layer and washed with water
25 yielded a red thick oil.

Preparation of a radiation curable composition
comprising a monofunctional maleimide of Ex. I or IV:

5 A radiation curable composition was prepared by mixing 1 wt.% of the compound X in Table 1 with 1 wt.% of N,N-dimethylethanolamine and 98 wt.% of an tetrafunctional polyester acrylate oligomer (Ebecryl®80 from UCB).

10 A coating was applied on a glass substrate using a variable thickness doctor blade, wire wound applicator (e.g. 200 µm 'K-bar') and the coating was cured by UV light (N₂, 2.2 J/cm²), using a Fusion H-bulb lamp (6 kW).

15

Table 1:

composition comprising maleimide from	König hardness (s)
(Example I)	63.0
(Example IV)	71.4

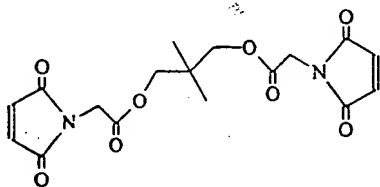
20 These data show that the presence of a monomaleimide compound in a coating composition results in a radiation-curable coating, which is properly cured upon radiation.

25 Examples VII to XX are related to the preparation and characterisation of multifunctional maleimide compounds with 1 methylene spacer group between the maleimide group and the functional group. Further, the use of said

maleimides in a radiation-curable composition comprising said maleimides is given.

Example VII

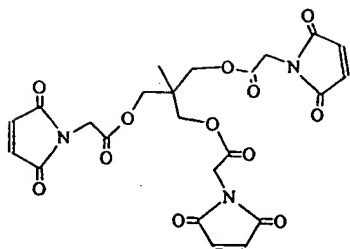
5 Preparation of a bis-maleimide from 2,2-dimethylpropanediol



3.15g (30.2mmol) 2,2-dimethylpropanediol was dissolved
10 in 75ml THF, 5.0ml (64mmol) pyridine (and tert. butyl
catechol) were added. [In the synthesis, generally
about 10-50 mg tert. butyl catechol was used]. After
cooling down to -10°C 10.5g (60.5mmol)
N-[(chloroformyl)methyl] maleimide dissolved in 75ml
15 THF was added slowly to the solution. After stirring
overnight, filtration, extraction with water/ether,
drying, decoloring and evaporation an orange oil was
collected. The orange oil became a wet solid after
adding ether.
20 After crushing and drying in a vacuumoven 3.45g (9mmol,
30%) of a white/light yellow solid was obtained.
¹H-NMR CDCl₃ (δ/ppm): 6.8(s, 4H); 4.3(s, 4H); 3.9(s, 4H);
0.95(s, 6H)

25 Example VIII

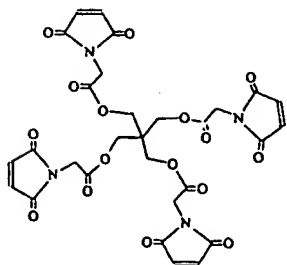
Preparation of a tris-maleimide from tris-
(hydroxymethyl)ethane



- To 1.80g (15mmol) 1,1,1-tris(hydroxymethyl)ethane dissolved in 100ml THF 6.5ml (46mmol) triethylamine and
- 5 tert. butyl catechol were added. After cooling to -10°C 8.0ml (46mmol) N-[(chloroformyl) methyl] maleimide dissolved in 50ml THF was added dropwise. After stirring for three hours at room temperature the reaction mixture was filtered off, evaporation of the
- 10 orange filtrate yielded a sticky solid which was suspended in ether. After filtration, washing with ether/water and drying in the vacuum oven 6.8g (12.8mmol, 85%) of a pale white powder was obtained .
- $^1\text{H-NMR}$ CDCl_3 , (δ/ppm): 6.76(s, 6H); 4.25(s, 6H);
- 15 3.95(s, 6H); 0.95(s, 3H)

Example IX

Preparation of a tetra-maleimide from pentaerythritol

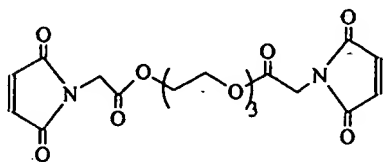


- 20 2.72g (20mmol) pentaerythritol, tert. butyl catechol and 25ml (180mmol) triethylamine were dissolved in 75ml

THF. After cooling to -10°C 14.5gram (84mmol) N-
[(chloroformyl)methyl] maleimide dissolved in 50ml THF
was added dropwise. After stirring overnight at room
temperature the brown suspension was quenched with
5 water and filtered off. The brown residu contained the
amine salt as well as the desired product. Several
washings with water and drying in the vacuumoven
yielded 5.5g (8mmol, 40%) pale white/brownish powder.
 $^1\text{H-NMR}$, $\text{dms}\text{-d}_6$ (δ/ppm): 7.15(s,2H); 4.3(s,2H);
10 4.1(s,2H);
melting point: 162-165°C

Example X

Preparation of a bis-maleimide from triethyleneglycol



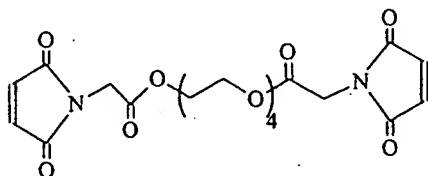
15 7.5g (50mmol) triethyleneglycol was dissolved in 150ml
dimethylcarbonate. 14.0ml (100mmol) triethylamine and
tert. butyl catechol were added while the mixture was
cooled to 0°C. 17.4g (100mmol) of N-
20 [(chloroformyl)methyl] maleimide dissolved in 50ml
dimethylcarbonate was added dropwise. After the
reaction was stirred overnight at room temperature it
was filtrated off and the filtrate was evaporated. The
oil which was obtained crystallised after the addition
25 of ether (150 ml) 15.2grams (35.8mmol, 72%) of a yellow
powder was obtained. When repeating this experiment
with 50% higher amounts, a yield was obtained of 80%.

$^1\text{H-NMR}$, CDCl_3 , (δ/ppm): 6.8 (s, 4H); 4.3 (d, 8H); 3.7 (q, 8H)

$^{13}\text{C-NMR}$ CDCl_3 , (δ/ppm): 135 (C=C); 78.5 (t, quart. C);
68.5 (t, CH_2);

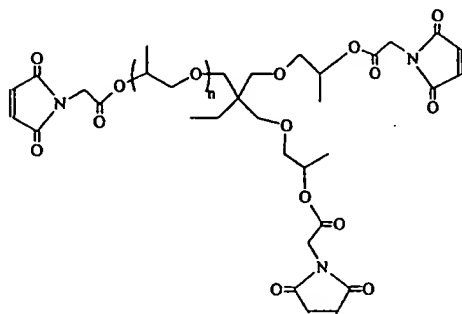
5 Example XI

Preparation of a bis-maleimide from tetraethyleneglycol



- 4.85g (25mmol) tetraethyleneglycol was dissolved in 100ml THF. When 7.0ml (50mmol) triethylamine and tert. butyl catechol were added, the solution was cooled to $<0^\circ\text{C}$. 8.7g (50mmol) of N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise. After stirring overnight at room temperature the suspension was filtered and evaporated. Extraction with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ yielded 9.4grams (20mmol) of a dark brownish oil.

$^1\text{H-NMR}$, CDCl_3 , (δ/ppm): 6.75 (s, 4H); 4.25 (t, 8H);
3.65 (q, 12H)

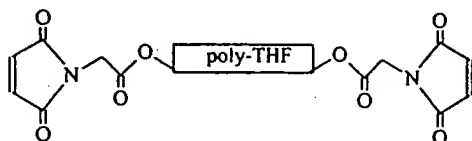
Example XIIPreparation of a tris-maleimide from propoxylated trimethylolpropane

- 5 11.4g (37mmol) propoxylated trimethylolpropane (1PO/OH) was dissolved in 200ml THF. 9.1ml (112mmol) pyridine and tert. butyl catechol were added while the solution was cooled to -10°C.
- 10 19.5g (112mmol) N-[(chloroformyl)methyl] maleimide dissolved in 80ml THF was added dropwise over three hours. The reaction was stirred at room temperature during the night. After filtration the clear pink solution was washed two times water and with saturated NaCl. Drying on Na₂SO₄, filtration and evaporation
- 15 resulted in a yellow oil with red spots in it. Dissolving in dichloromethane, filtration and evaporation yielded 20grams (27.8mmol, 75%) of a yellow oil.

¹H-NMR, CDCl₃ (δ/ppm): 6.85(s, 6H); 5.0(m, 3H); 4.2(s, 6H);
20 3.3(m, 12H); 1.3(m, 2H); 1.15(d, 9H); 0.775(t, 3H)

Example XIII

Preparation of an α,ω -hydroxy polytetrahydrofuran-650 functionalised with two maleimide end groups

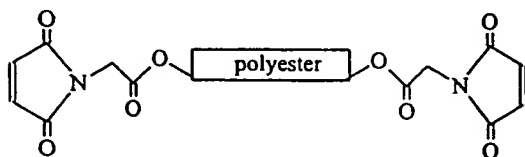


- 5 12.85g (20mmol) α,ω -hydroxy-polyTHF-650 was dissolved in 125ml THF. 6.0ml (43mmol) triethylamine and tert. butyl catechol were added while the solution was cooled to -10°C . 7.0g (40mmol) N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added in 45
- 10 minutes. After stirring overnight at room temperature, filtration and evaporation the oil was extracted with ether/ H_2O .
- The product was collected as a orange oil with a yield of 8.4grams (9.1mmol, 45.4%).

15

Example XIV

Preparation of a bis-maleimide functionalised polyester



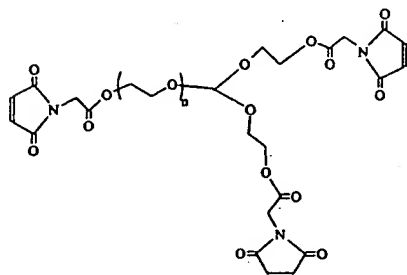
- 20 73g (43meq) hydroxyfunctional aromatic polyester (no ethylenical unsaturations) was dissolved in 250ml THF. 5.75ml triethylamine and tert. butyl catechol were added while the solution was cooled to 0°C . To the vigorously stirred solution N-[(chloroformyl)methyl]

maleimide dissolved in 50ml THF was added. The reaction was stirred overnight at room temperature evaporated and extracted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$.

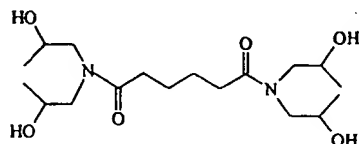
Over 50g of the polyester functional maleimide was
5 obtained as a orange oil which contains a few percentages of high boiling aromatic solvent.

Example XV

Preparation of a tris-maleimide from ethoxylated 10 glycerol

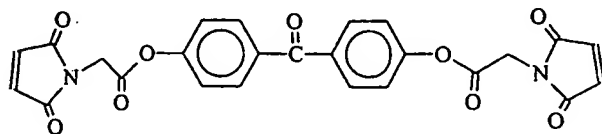


14g (14mmol) ethoxylated glycerol, tert. butyl catechol and 7.0ml (50mmol) triethylamine were dissolved in 150ml THF and cooled to -10°C . N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise. The
15 reaction was filtered and evaporated after stirring overnight at room temperature. The dark residu was extracted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ and 12.9g (9mmol, 64%) of a dark brown oil was obtained.

Example XVITetra-maleimide from m-Primid®

5

4.7g (12.5mmol) m-Primid® (see formula) was suspended in 100ml chloroform. 7.0ml (50mmol) triethylamine and tert. butyl catechol were added. The well stirred mixture was cooled to 0°C and 8.7g (50mmol) N-
10 [(chloroformyl) methyl] maleimide dissolved in 60ml CHCl₃ was added dropwise over two hours. After the reaction was stirred overnight at room temperature no amine hydrochloric acid salts were precipitated. Extraction with water yielded 10g (10.8mmol, 86%) of a
15 green/yellow oil.

Example XVIIPreparation of 4,4' bis-maleimide benzophenone

20

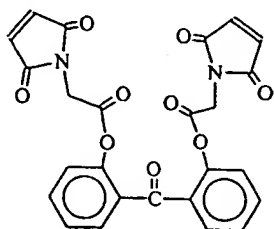
5.35g (25mmol) of 4,4-dihydroxybenzophenone was dissolved in 195ml THF. Triethylamine (7ml) tert. butyl catechol were added and the mixture was cooled to -20°C. N-[(chloroformyl)methyl]maleimide (8.7g, 50mmol),
25 dissolved in 50ml THF was added dropwise. The reaction

mixture was stirred overnight at room temperature. The white suspension was filtered, the filtrate was evaporated and the obtained white-light rose powder was dried and pulverized to yield 3.7g product.

5

Example XVIII

Preparation of 2,2'-bis-maleimide benzophenone



In an analogous way to example XI starting with 2,2'-
10 dihydroxybenzophenone, the compound aimed at was obtained. After the overnight reaction, the solvent was removed by N_2 -flow, and the red solution was filtered and the filtrate evaporated. The so obtained oil was dissolved in 200 ml CH_2Cl_2 , and the salmon-rose solution
15 was extracted twice with 40ml 10% HCl, and four times with 40ml H_2O . After drying and evaporation of the solvent, 4.4g product was obtained.

Example XIX

Preparation of a bis-maleimide from hydroxy functional hydrogenated polybutadiene

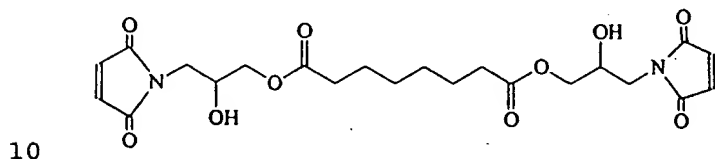
Hydrogenated polybutadiene 1.19 meq/g OH, $M_w = 1000$ (21g) was dissolved in 300ml THF and cooled to $-10^\circ C$ after addition of 5 ml triethylamine and tert.
25 butyl catechol. The N-[(chloroformyl)methyl] maleimide (5g), dissolved in THF was slowly added dropwise. After

stirring overnight at room temperature and filtration, the filtrate was evaporated, dissolved in CH_2Cl_2 and extracted with 30ml H_2O .

After drying and evaporating, the product was obtained
5 as an orange oil in an amount of 12g.

Example XX

Reaction of the epoxy maleimide with a di-acid (bis-maleimide from suberic acid)



Suberic acid (2.6g) and epoxymaleimide (4.6g) were dissolved in 100 ml CHCl_3 .

The reaction was catalysed using $\text{Et}_4\text{N}^+\text{Br}^-$. Stabiliser
15 was tert. butyl catechol. The reaction mixture was refluxed for 4 hr, and thereafter was left stirring over the week and at room temperature. The mixture was refluxed for a few hours, cooled, some residue was filtered of and the filtrate was evaporated to yield 6g
20 product.

Use of maleimide compounds of Ex. XII, X, XVII, VII, VIII and XIV respectively in a radiation curable composition:

25

- A radiation curable composition was prepared by mixing 2 wt.% of the compound obtained in example XII with 98 wt.% of a tetrafunctional polyesteracrylate

(Ebecryl®80 from UCB).

A coating was applied on a glass substrate using a 150 µm K-bar and the coating was cured by UV light (1 J/cm², using a Fusion H-bulb lamp under N₂ atmosphere.

A test specimen was cut from the cured film (3x4 cm), and acetone extractables were measured by 24 hr extraction in 100 ml acetone. The weight of the sample was measured before and after extraction, and the weight loss determines the amount of extractables.

To determine the type of extractable compounds, the acetone was evaporated and the residue was analysed with 200 MHz ¹H-NMR. From this analysis, the ratio of acrylate functional extractables and non-acrylate extractables could be determined.

The cured coating did have 4 wt.% of extractables, which were mainly acrylates. Only about 0.1 wt.% or less was non-acrylate, which means that only about 5% of the photoinitiator appeared to be extractable.

In contrast, if the same acrylate resin is cured with 2 wt.% of Irgacure 184 (a type-I photoinitiator), the cured coating exhibited 5 wt.% of extractables, of which 1.2 wt.% originated from the photoinitiator (hence, 60% of the photoinitiator appeared to be extractable from the cured product).

In case the same acrylate resin was cured using a conventional type II initiating system (benzophenone with an amine synergist), also 60% of the photoinitiating system appeared to be extractable.

- Coating compositions were prepared with 1 wt.% of the triethyleneglycol bismaleimide of example X, 1 wt.% of

N-methyl diethanolamine and 98% of acrylate (Ebecryl P-36, 80, 83 or 810) according to Table 2. Coatings were prepared and cured as described above. The König hardness was measured, results are given in Table 2.

5

Table 2

Resin*	König hardness(s) of coating**
Ebecryl® P-36	9.8
Ebecryl® 80	74.2
Ebecryl® 83	26.6
Ebecryl® 810	32.2

- Ebecryl® 36: 86% acrylated oligomer; 14 wt.%
10 diethylene glycol diacrylate
- Ebecryl® 80: amine modified polyether acrylate
(tetrafunctional)
- Ebecryl® 83: amine modified polyether acrylate
(tetrafunctional)
- 15 Ebecryl® 810: polyester acrylate

** coating: 1 wt.% Ex. X + 1 wt.% N-methyldiethanolamine + 98 wt.% resin*

- 20 - The compound of Example XVII was used in 1 wt.% with 99 wt.% Ebecryl 83, curing with 1 J/cm² resulted in a coating with a König hardness of 81 s.

- The Maleimide compounds (1 wt.%) given in Table 3

were mixed with 1 wt.% of N,N-dimethylethanolamine and 98 wt.% Ebecryl®80.

Table 3

5

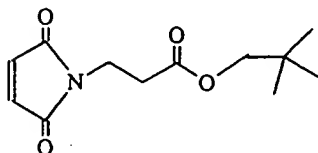
Maleimide From	König(s)
Example VII	74.2
Example XIII	57.4
Example XIV	46.2

Examples XXI and XXII are related to the preparation and characterisation of a monofunctional maleimide compound with more than 1 methylene spacer group
10 between the maleimide group and the functional group and to the preparation of a radiation-curable composition comprising said maleimide.

Example XXI

15

Preparation of a monofunctional maleimide from neopentyl alcohol:



40 mmol 2,2-dimethyl-1-propanol was dissolved in 175 ml dry tetrahydrofuran. 40mmol
20 triethylamine and tert-butyl catechol were added. The mixture was cooled to 0°C and 40 mmol N-[(chloroformyl)ethyl]maleimide dissolved in 50 ml tetrahydrofuran was slowly dropped to the solution. The reaction mixture was stirred overnight at room

temperature. After filtration and evaporation, a pale orange liquid residu was obtained. Cooling in a cold acetone bath, and drying in a vacuum oven yielded 30.7 mmol of a solid product.

5 Example XXII

Preparation of a radiation curable composition comprising a maleimide compound:

A radiation curable composition was
10 prepared by mixing 1 wt.% of the maleimide compound of Example I with 1 wt.% of N,N-dimethylethanolamine and 98 wt.% of an tetrafunctional polyester acrylate oligomer (Ebecryl®80 from UCB).

A coating was applied on a glass substrate
15 using a variable thickness doctor blade, wire wound applicator (e.g. a 200 µm 'K-bar') and the coating was cured by UV light (N_2 , 2.2 J/cm²), using a Fusion H-bulb lamp.

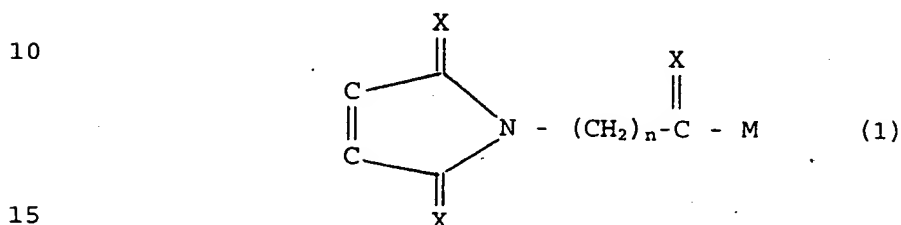
The cured coating exhibited a König
20 hardness of 65.8 s.

This shows that the presence of such a maleimide compound in a coating composition results in a radiation-curable coating, which is properly cured upon radiation.

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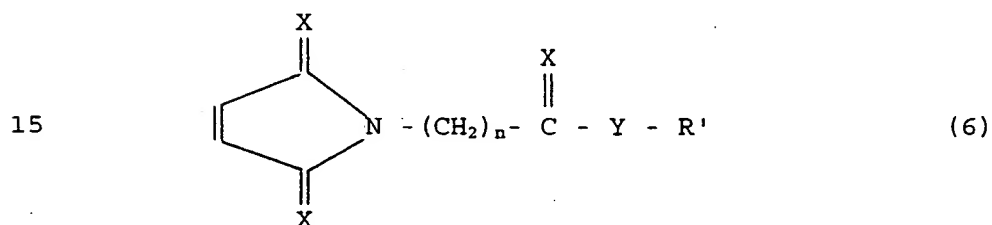
CLAIMS

1. Process for the preparation of a maleimide compound comprising the steps of
- (i) reacting a compound according to formula (1)



- wherein M is halogen or alkoxylate, and each X, independently, is O or S, with
- 20 a compound (2) comprising a backbone and having at least 1 group per molecule, capable of reacting with the compound according to formula (1), and
- (ii) obtaining the maleimide compound.
- 25 2. Process according to claim 1 wherein the maleimide compound is monofunctional.
3. Process according to claim 2 wherein n is equal to 1 and wherein said backbone is not comprising benzophenone, a succinimide or a phenyl group.
- 30 4. Process according to claim 2 wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 169 and is not comprising an anhydride or cyclodextrine group.
5. Process according to claim 1 wherein the
- 35 maleimide compound is multifunctional.

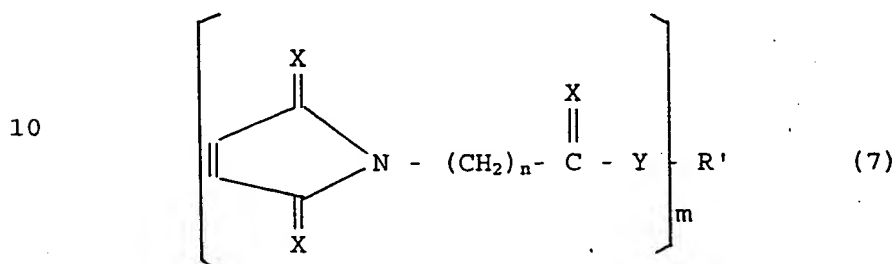
6. Process according to claim 5 wherein n is equal to 1.
7. Process according to claim 5 wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 150 and does not comprise a nitrogen containing phenyl group.
8. Process according to any one of claims 1-7 wherein each X is oxygen.
9. Monofunctional maleimide compound according to formula (6)



- 20 wherein Y is O, S or NH; each X, independently, is O or S; and R' is the remainder of the backbone, and wherein
- (i) n equals 1 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and not comprising benzophenone, a succinimide or anhydride group, or
- 25 (ii) n equals 2 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and said backbone is not comprising a diol-substituted alkane, a succinimide, anhydride or cyclodextrine group, or
- 30 (iii) n is at least 3.
10. Monofunctional maleimide compound according to claim 9 wherein the molecular weight of the monofunctional maleimide compound is from about 159 to about 100,000.
- 35

11. Monofunctional maleimide compound according to any one of claims 9-10 wherein the molecular weight of the monofunctional maleimide compound is from about 173 to about 10,000.

5 12. Multifunctional maleimide compound according to formula (7)



15 wherein Y is O, S or NH, R' is the remainder of the backbone, and m is - on average - 1.6 or higher, and wherein

(i) n equals 1 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons, or

20

25

(ii) n is at least 2 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)ether, (oligo)ester, (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons.

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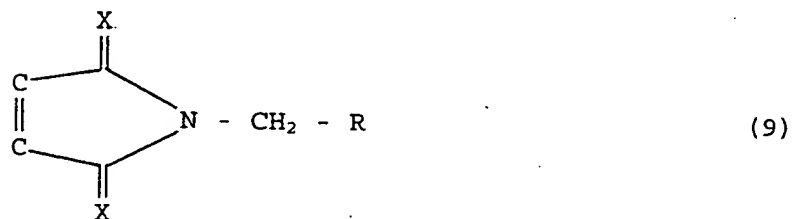
13. Multifunctional maleimide compound according to claim 12 wherein the compound has a functionality

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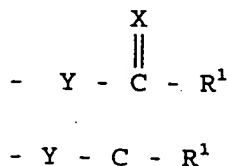
wherein at least R^1 or R^2 is the remainder of the molecule.

17. Radiation-curable composition comprising
- a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b)
 - b) at least one maleimide compound according to any one of claims 9-14 or 16.

18. Radiation-curable composition comprising
- a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b)
 - b) at least one multifunctional maleimide compound having on average at least 1.6 maleimide groups according to formula (9)



wherein R is



wherein

each X, independently, is O or S

Y is O, S or NH, and

wherein R^1 is the remainder of the backbone of the multifunctional maleimide compound.

19. Composition according to any one of claims 17-18

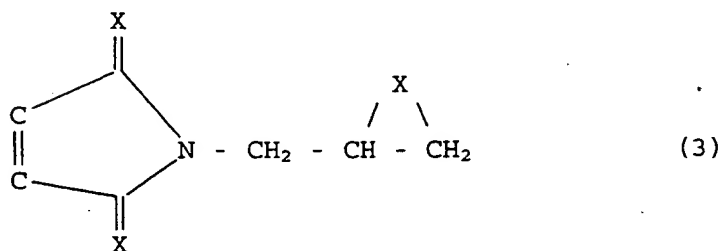
of 1.9 or higher.

14. Multifunctional maleimide compound according to any one of claims 12-13 wherein the molecular weight of the maleimide compound is from about 250 to about 100,000.

15. Process for the preparation of a maleimide compound comprising the steps of
(i) reacting a compound according to formula (3)

10

15



20

wherein X, independently, is O or S,
with

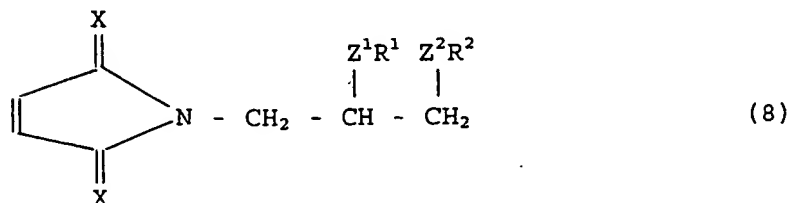
a compound (4) having at least on average 1 group per molecule, capable of reacting with the compound according formula (3) and

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- (ii) obtaining the maleimide compound.

16. Maleimide compound according to formula (8)

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comprising at least one maleimide group, wherein X is O or S, and Z¹ and Z² independently designate for O, S, or NR³, and wherein R¹, R² and R³ can be, independently, hydrogen or an organic group and

wherein the composition comprises conventional photoinitiators or photosensitizers, or mixtures thereof.

- 5 20. Product coated with a cured coating which coating before curing is a coating composition according to any one of claims 17-19.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

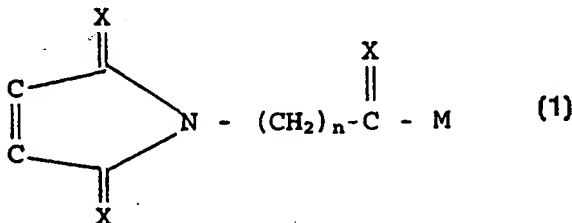
(51) International Patent Classification ⁷ : C07D 207/44, C08F 290/14, 222/40		A3	(11) International Publication Number: WO 00/10974
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(71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).			
(72) Inventors; and		Published	
(75) Inventors/Applicants (for US only): DIAS, Aylvin, Jorge, Angelo, Athanasius [GB/NL]; Sphinxlunet 11 F, NL-6221 JD Maastricht (NL). JANSSEN, Johan, Franz, Gradus, Antonius [NL/NL]; Marisstraat 11, NL-6165 AP Geleen (NL). VAN DIJCK, Michael, Alphonsus, Cornelis, Johannes [NL/NL]; Schuttersdreef 16, NL-6181 DR Stein (NL). TUSSEN, Pascal, Maria, Hubert, Pierre [NL/NL]; Oranjesingel 88, NL-6191 XV Beck (NL).		With international search report.	
(74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph; DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).		(88) Date of publication of the international search report: 15 June 2000 (15.06.00)	

(54) Title: PROCESS FOR THE PREPARATION OF A MALEIMIDE COMPOUND, MALEIMIDE COMPOUND, RADIATION-CURABLE COMPOSITIONS COMPRISING SAID COMPOUND AND COATED PRODUCTS

(57) Abstract

The invention relates to a process for the preparation of a maleimide compound comprising the steps of (i) reacting a compound according to formula (1) wherein M is halogen or alkoxylate, and each X, independently, is O or S, with a compound (2) comprising a backbone and having at least 1 group per

molecule, capable of reacting with the compound according to formula (1), and (ii) obtaining the maleimide compound.



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INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07D207/44 C08F290/14 C08F222/40		International Application No PCT/NL 99/00523
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07D C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OISHI T ET AL: "SYNTHESIS AND POLYMERIZATION OF MALEIMIDES CONTAINING PERFLUOROALKYLGROUPS" POLYMER JOURNAL, JP, SOCIETY OF POLYMER SCIENCE, TOKYO, vol. 26, no. 5, 15 May 1994 (1994-05-15), pages 613-622, XP000452191 ISSN: 0032-3896 page 614, column 1 abstract <div style="text-align: center;">--- -/--</div>	1,9,18
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier documents but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">10 February 2000</div>		Date of mailing of the international search report <div style="text-align: center;">21/02/2000</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center;">Paisdor, B</div>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 99/00523

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OATIS J E ET AL: "Synthesis and Photochemistry of Two Cleavable Heterobifunctional Benzophenone Protein Crosslinkers" TETRAHEDRON LETTERS,NL,ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, vol. 39, no. 13, 26 March 1998 (1998-03-26), pages 1665-1668, XP004108443 ISSN: 0040-4039 page 1665 ---	1,9
X	US 5 204 366 A (LAVANISH JEROME M ET AL) 20 April 1993 (1993-04-20) column 13 -column 14; examples 53-58 ---	1,9
X	KOTTNER N ET AL: "INVESTIGATIONS ON THE SYNTHESIS OF POLYIMIDES WITH CORONAND STRUCTURE VIA TANDEN DIELS-ALDER ADDITION POLYMERIZATION" ANGEWANDTE MAKROMOLEKULARE CHEMIE. APPLIED MACROMOLECULAR CHEMISTRY AND PHYSICS,DE,WILEY VCH,WEINHEIM, vol. 254, 1 February 1998 (1998-02-01), pages 39-45, XP000752131 ISSN: 0003-3146 the whole document ---	1,9,12, 17
X	J R COGGINS: "Crosslinking agents for proteins" PROTEINS LABFAX,1996, pages 307-314-314, XP002091998 page 309; table 2 page 310; table 3 ---	1,9
X	WO 98 07759 A (JOENSSON E SONNY ;HOYLE CHARLES E (US); CLARK SHAN CHRISTOPHER (US) 26 February 1998 (1998-02-26) page 7 -page 9; claims ---	1,9,12, 17-20
X	US 5 274 119 A (FRAZIER KEVIN A ET AL) 28 December 1993 (1993-12-28) column 3 column 6 column 13 -column 14 column 19 -column 20 ---	1,9,12
A	US 4 980 482 A (FRAZIER KEVIN A) 25 December 1990 (1990-12-25) the whole document ---	1,9,12, 18
P,X	EP 0 878 482 A (DAINIPPON INK & CHEMICALS) 18 November 1998 (1998-11-18) page 18 -page 47; claim 1; examples -----	1,9,12, 18

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NL 99/00523

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty of the product claims 9, 12 and 16. So many documents were retrieved that it is impossible to determine which parts of the aforementioned claims may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claims is impossible. For the definition of the the compound claims funtional features, and not clearly defining structural features were used. Consequently, the search has been restricted to the type of "organic backbones, or organic groups" being present in the examples and on the inventive concept underlying the present application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00523

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5204366 A	20-04-1993	EP 0608445 A US 5310937 A	03-08-1994 10-05-1994
WO 9807759 A	26-02-1998	AU 4085797 A	06-03-1998
US 5274119 A	28-12-1993	NONE	
US 4980482 A	25-12-1990	NONE	
EP 0878482 A	18-11-1998	JP 11124403 A JP 11124404 A AU 1586499 A WO 9948928 A	11-05-1999 11-05-1999 18-10-1999 30-09-1999